fonic acid and 10 ml. of thionyl chloride in a flask with a glass joint reflux condenser was heated at the refluxing temperature of the latter compound for two hours. After cooling, the thionyl chloride was removed by distillation and the residue dried at room temperature and 1.0 mm. pressure for two hours. The **propane-1,3-disulfonic acid** so obtained weighed 0.91 g., was a light gray powder that melted at 120–124°, and had a neutral equivalent of 103 (calcd. 102).

Anal. Calcd. for $C_3H_8O_6S_2$: S, 31.4. Found: S, 31.3.

A sample of ethane-1,2-disulfonic acid dihydrate, m. p. 110–112°, treated in a similar manner was quantitatively converted into the anhydrous acid, m. p. 172–174°. A 0.68-g. sample of the dihydrate after twelve hours refluxing with thionyl chloride was converted into 0.51 g. (97%) of the ethane disulfonic anhydride, m. p. 140–143°; neutral equivalent 88. By a similar treatment the hydrated propane-1,3-disulfonic acid was converted into the corresponding anhydride, m. p. 194–196°; neutral equivalent, 94.5.

Summary

The properties of the anhydrous ethane-1,2- and propane-1,3-disulfonic acids are described. Each of these acids may be converted into the corresponding cyclic anhydride either by heat or by the action of thionyl chloride.

Ethane-1,2-disulfonyl chloride is converted by fuming sulfuric acid into the parent disulfonic acid.

The esterification of ethane-1,2-disulfonic acid and ethylenesulfonic acid is satisfactorily accomplished with ketene diethylacetal.

MADISON, WISCONSIN RECEIVED JUNE 20, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RALPH L. EVANS ASSOCIATES]

N-Alkylethylenediamines

BY FRED LINSKER AND RALPH L. EVANS

Since the direct monoalkylation of ethylenediamine had been reported as unsuccessful by Schneider,[1] the synthesis of alkylethylenediamines was repeatedly attempted through indirect methods. A summary of the previous work in this field is given by Aspinall,[2] who in the same paper presented a novel approach to the problem.

Recently it was observed in this Laboratory[3] that reactive aromatic halogen compounds such as *o*- and *p*-nitrochlorobenzene could be condensed with substantially anhydrous ethylenediamine to give good yields of the expected mono- and *sym*-di-N-substituted ethylenediamines depending upon the ratio of starting materials used. In accordance with these findings it was believed that alkyl halides would react in a similar fashion with anhydrous ethylenediamine and a series of experiments was conducted to verify this assumption.

Diverging from Schneider's unsuccessful use of alkyl iodides on 70% ethylenediamine, we worked with alkyl chlorides and bromides and highly concentrated (95%) ethylenediamine. The latter can be prepared easily by several convenient methods from the commercially available (65–70%) product. Recommended are the dehydration with sodium hydroxide[4] and the heat decomposition of the ethylenediamine–zinc oxalate compound.[5]

Experimental

Preparation.—The condensation may be effected by refluxing the mixture of the two components as such or in a solvent such as ethyl alcohol or *n*-butanol. A large excess of ethylenediamine is used in order to avoid the formation of other than the monoalkyl derivatives and to bind the hydrochloric acid which is formed in the reaction. The procedure followed for N-*n*-octyl-ethylenediamine is typical. To 5 g. (0.08 mole) of ethylenediamine (95%) and 3.1 g. (0.02 mole) of *n*-octyl chloride was added sufficient absolute ethyl alcohol (40 cc.) to dissolve the two immiscible liquids. The solution was refluxed for three hours in an oil-bath and ethyl alcohol was evaporated, causing the residual liquid to separate into two layers. The upper layer was separated, 30 cc. of water added and the precipitated white solid was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent evaporated; yield 3 g. In order to remove the last traces of unchanged ethylenediamine, the crude product was suspended in 20 cc. of water and the ether extraction repeated.

The dihydrochloride was prepared by bubbling dry hydrogen chloride through the solution of the base in dry ether.

The dipicrate was formed in alcoholic medium and recrystallized in this case from water; in all other cases from alcohol.

While in the case of the saturated alkyl halides studied, the reaction proceeds smoothly to give excellent yields of the desired products, allyl chloride reacts very vigorously with ethylenediamine, the yield of allylethylenediamine being only 28% of the theoretical. This may be due to side reactions occurring at the double bond. In this case the allyl chloride (38 g.) was added slowly with stirring to 130 g. of 95% ethylenediamine. The resulting solution was heated to reflux temperature for thirty minutes and distilled under atmospheric pressure. Most of the liquid distilled at 117–137° and a crystalline residue remained in the flask. The distillate was fractionated and the fraction boiling at 160–170° was collected (13.6 g.).

In order to obtain the dihydrochloride 1 g. of base was dissolved in 3 cc. of ethyl alcohol and 1 cc. of concentrated hydrochloric acid was added. The mixture was evaporated to dryness and the residue recrystallized from alcohol-acetone.

Properties

The free bases from octyl up are low-melting, white, waxy solids, insoluble in water, soluble in alcohol, ether, benzene and chloroform. They form dipicrates and combine with two acid equivalents to yield neutral salts. The dihydrochlorides, sulfates, and dinitrates are sparingly soluble in water, but the diacetates and some other salts with organic acids dissolve readily in this solvent. The solutions of these "soaps in reverse" show lowered

---

[1] Schneider, *Ber.*, **28**, 3073 (1895).

[2] Aspinall, THIS JOURNAL, **63**, 852 (1941).

[3] Linsker and Evans, *J. Org. Chem.*, in press.

[4] Wilson, *Ind. Eng. Chem.*, *Ind. Ed.*, **27**, 868 (1935).

[5] John C. Bailar, Jr., THIS JOURNAL, **56**, 955 (1934).

TABLE I

N-ALKYLETHYLENEDIAMINES, $RHNCH_2CH_2NH_2$

R	M. p., °C.	Yield, %	Formula	Dihydrochloride M. p., °C.	Dihydrochloride % Carbon Calcd.	Dihydrochloride % Carbon Found	Dihydrochloride % Hydrogen Calcd.	Dihydrochloride % Hydrogen Found	Dipicrate M. p., °C.	Dipicrate % Carbon Calcd.	Dipicrate % Carbon Found	Dipicrate % Hydrogen Calcd.	Dipicrate % Hydrogen Found
Allyl	(*a*)	28	$C_5H_{12}N_2$	173-175	34.62	34.22	8.10	8.09	149-150	36.56	36.50	3.23	3.40
n-Octyl[b]	29-31	84	$C_{10}H_{24}N_2$	208-210	49.00	48.91	10.61	10.45	131-132	41.90	41.70	4.76	4.35
n-Decyl	36-37	83	$C_{12}H_{28}N_2$	220-222	52.75	52.65	10.99	10.77	144-145	43.76	43.70	5.16	5.15
n-Dodecyl[b]	36-38	98	$C_{14}H_{32}N_2$	222-224	55.81	55.45	11.29	11.47	141-142	45.48	45.60	5.54	5.69
n-Tetradecyl	42-43	91	$C_{16}H_{36}N_2$	198-199	58.36	58.77	11.55	11.40	117-119	47.05	47.23	5.88	6.12
n-Hexadecyl	55-57	94	$C_{18}H_{40}N_2$	204-206	60.50	61.00	11.76	11.37	130-131	48.52	49.00	6.20	6.00
n-Octadecyl[c]	64-65	92	$C_{20}H_{44}N_2$	194-196	62.34	62.20	11.95	12.18	124-126	49.87	49.36	6.49	6.92

[a] B. p. 156-158°. [b] Dipicrate yellow-green. [c] Base insoluble in ligroin, soluble in dioxane. Calcd. for $C_{20}H_{44}N_2$: C, 76.92; H, 14.10. Found: C, 76.91; H, 14.00.

surface tension and form stable foams. Like the parent compound, these substituted ethylenediamines form complex metal salts with the transition elements.

The dihydrochlorides, crystallized from alcohol, give white or colorless prisms, sparingly soluble in water, slightly soluble in cold alcohol, and insoluble in dilute hydrochloric acid and in organic solvents. They melt at a relatively high temperature with decomposition.

The dipicrates crystallized from alcohol give yellow or yellow-green prisms.

The physical and analytical data relative to these bases and their dihydrochlorides and dipicrates are collected in the table.

Summary

The even-numbered straight chain alkylethylenediamines from C_8 to C_{18} have been prepared by direct alkylation of ethylenediamine and have been characterized. They are waxy, low-melting solids which combine with two equivalents of mineral acid to form neutral salts whose solutions have low surface tension and show promise as detergents.

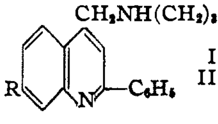
NEW YORK 17, N. Y. RECEIVED JUNE 22, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Synthesis of Some 2-Phenyllepidylamines[1]

BY D. S. TARBELL, J. F. BUNNETT, R. B. CARLIN AND V. P. WYSTRACH

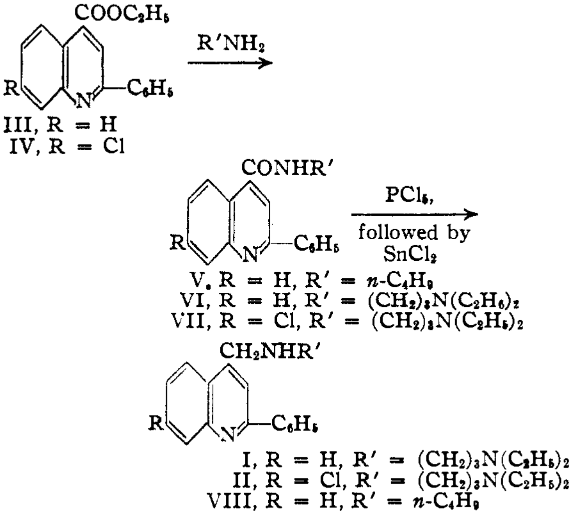
This paper reports the synthesis and properties of some 2-phenyllepidine derivatives containing 3-diethylaminopropylamino side chains on the methyl group, of the type shown.



I, R = H
II, R = Cl

One method of synthesis for this type of compound was developed by Work[2]; in attempting to prepare 4-quinolinealdehyde by the Sonn-Müller method from the corresponding anilide, he obtained N-phenyllepidylamine in good yield, instead of the expected aldehyde. This reaction was applied by him to the synthesis of some dialkylaminoalkyllepidylamines.[2a]

We have found that, by careful control of the experimental conditions, the reaction can be applied to the synthesis of 2-phenyllepidylamines, such as I and II. The steps involved are indicated below; the product formed by the action of phosphorus pentachloride on the amide is probably the amidodichloride,[2] and this intermediate is very sensitive to heat, so that operations must be carried out at temperatures below 80°.



III, R = H
IV, R = Cl

V, R = H, R' = n-C_4H_9
VI, R = H, R' = $(CH_2)_3N(C_2H_5)_2$
VII, R = Cl, R' = $(CH_2)_3N(C_2H_5)_2$

I, R = H, R' = $(CH_2)_3N(C_2H_5)_2$
II, R = Cl, R' = $(CH_2)_3N(C_2H_5)_2$
VIII, R = H, R' = n-C_4H_9

An attempt to apply this method to the synthesis of the 6-methoxy analog of I was unsuccessful; no pure product except starting material could be isolated from the treatment of the amide with phosphorus pentachloride and stannous chloride.

---

[1] The work described in this article was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Rochester.

[2] Work, *J. Chem. Soc.*, 429 (1942).

[2a] The preparation of secondary amines by reduction of the chloroimides with hydrogen and palladium has been described by Tishler, Wendler, Ladenburg and Wellman, THIS JOURNAL, **66**, 1328 (1944), and Bergel, Cohen and Haworth, *J. Chem. Soc.*, 165 (1945).